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Half-metallic magnetism in the 1990s

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The possibility of designing half-metallic magnetic multilayer systems is investigated. In part two the prospects of realizing a half-metallic antiferromagnet with emphasis on applications in scanning-tunneling microscopy is discussed.

1. Half-metallic magnetism as an interface property

PtMnSb is the material with the highest magneto-optical Kerr effect (MOKE) at ambient temperatures [1]. It is a half-metallic ferromagnet, i.e. it shows metallic conduction for one spin direction only [2]. This peculiar situation is responsable for the unusual magneto-optical properties. To appreciate this, a comparsion with the generation of spin-polarized electrons by laser irradiation of GaAs covered with Cs–O [3] may be helpfull (fig. 1). As the absorption of polarized light from the top of the spin–orbit-split valence band in GaAs leads to the emission of spin-polarized electrons, the absorption of light from the spin-polarized spin–orbit-split top of the valence band in PtMnSb leads to absorption of one polarization direction of the light only. This is responsable for the large contribution to the off-diagonal part of the dielectric tensor. So, the MOKE in PtMnSb and the creation of spin polarized electrons in GaAs are complementary phenomena, the similarity in electronic structure between the semiconducting spin direction in PtMnSb and III–V semiconductors was already stressed in ref. [2].

Other half-metallic magnets are NiMnSb [2], CoMnSb [4], FeMnSb [5], Fe_3O_4 [6], CrO_2 [7] and $KCrSe_2$ [8]. It should be stressed that half-metallic behaviour in itself cannot guarantee interesting MOKE properties. The optical transition in PtMnSb across the band gap is strong in PtMnSb (and, paradoxically, the origin of the strength is relativistic) [9]. It is an interesting question whether one can improve the MOKE in PtMnSb even further. A weak point in the properties of PtMnSb is that the optical excitations, responsable for the off-diagonal dielectric tensor, are limited to only a small fraction of the Brillouin zone, around the direct gap at Γ. If the top of the valence bands and/or the bottom of the conduction band were less disperse, one could hope to involve more electrons in the magneto-optical active transition. Attempts to achieve this by suitable doping have remained unsuccessful [10]. The reason for this is twofold. Most of the suggested systems could not be prepared. The ones which could be synthesized did not show an improvement in MOKE over PtMnSb. One has to realize that the MOKE is not only determined by the offdiagonal dielectric tensor σ but by the diagonal part ε_r as well:

$$\vartheta k + i\theta_k = c\,\frac{i\sigma}{\varepsilon_r^{1/2}(1-\varepsilon_r)}\,.$$

Doping possibly enhances σ but the substitutional disorder introduced by the doping has a deteriorative effect on ε, and it is not clear whether a net positive effect results. Some of the requirements of a good magneto-optical material relevant here are:
- the diagonal part of the dielectric tensor,
- the off-diagonal part of the dielectric tensor,
- a high Curie temperature,
- a sizable magnetic anisotropy.

It is questionable whether doping in order to

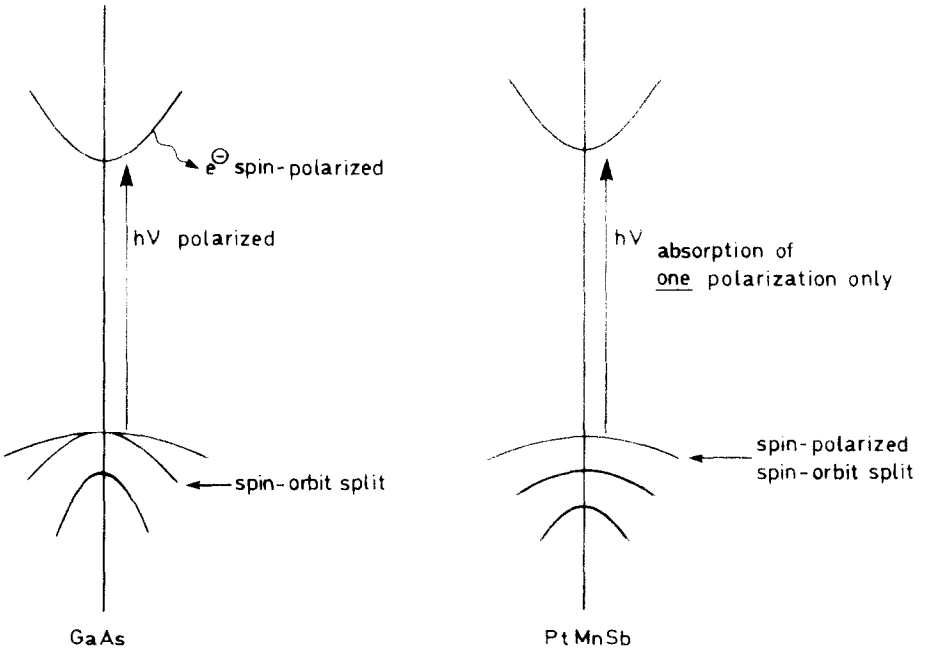

Fig. 1. The relation between the generation of spin-polarized electrons and MOKE in PtMnSb. (a) excitation from a spin-orbit split valence band by polarized light leads to the emission of spin-polarized electron. (b) excitation from a spin-orbit split spin-polarized valence band leads to the absorption of one polarization exclusively.

improve on one of these without any control over the others, while at the same time the stability of the suggested phases is dictated by thermodynamics (and thus also out of control of men) is a fruitful line of attack.

A new challenge is formed by the advance in the syntheses of metastable materials with techniques like molecular beam epitaxy (MBE). The feasibility emerges to put atoms where man decides rather than where thermodynamics dictates. At the moment control is limited in practice to one dimension, thus we are considering multilayer materials. These materials form an enormous challenge to the computational physicist: it extends his responsibility from the explanation of an unusual phenomenon in a given system to the prediction of systems with unusual properties. This area is one of the many pioneered by Art Freeman and his collaborators [11]. The question we like to answer here is: can we design multilayer systems made out of alternating layers of a semiconductor and a (ferro)magnetic metal with – as a result – half-metallic magnetic behaviour as an interface property? If the answer is yes one can hope to optimize the magneto-optical properties like the frequency at which the Kerr rotation peaks (related to the band gap of the semiconductor), the peak height (related to the oscillator strengths across the gap of the semiconductor), and the Curie temperature (related to the magnetic properties of the metal) *independently* by selecting suitable semiconducting and metallic constituents. As a free gift one obtains the required magnetic anisotropy because of the symmetry of the materials (PtMnSb, as a cubic material does not show the required anisotropy).

As a first attempt we focus on the multilayer system PbO/Fe. The motivation for this choice is as follows. As is well known, band structure calculations employing the local density approximation (LDA) underestimate the band gap of most semiconductors.

Since it is expected that the possible occurrence of half-metallic behaviour can depend critically on the correct description of the band gap

in the semiconducting phase, it is important to have a proper band gap in the calculation. The errors induced by the LDA can be corrected by the self-energy corrections in the G–W formalism. A relativistic calculation this way on a complicated system like a multilayer is at the moment out of reach (at least with the computers available to me). In order to circumvent this problem we select the semiconductor from a class of compounds where LDA systematically gives a good description of the band gap: the group IV-a divalent chalcogenides. Pb was selected because of its heavy mass (MOKE is relativistic in origin); PbO was selected because it has the largest band gap of the lead-chalcogenides. Figure 2 shows the calculated bandstructure of the low-temperature form of PbO, litharge, using the ASW method [12]. The valence band is in good agreement with the results obtained by Hoffman et al. [13], the band gap (1.70 eV) is in excellent agreement with experiment (1.71 eV) [14]. This is somewhat fortuitous, usually a less perfect agreement is found in these systems. As a ferromagnetic metallic constituent we select iron. It shows only a moderate misfit if PbO 0 0 1 is sandwiched with 1 1 0 iron and its high Curie temperature gives hope that the finite-temperature depolarization is still modest at room temperature. Figure 3 shows the electronic structure of a 1 : 1 Fe–PbO coherent interface. For didactic purposes in preparing the figure we have left out the offdiagonal interactions of the spin–orbit operator (L^+S^- and L^-S^+). The effect of this is remarkably small in view of the strength of the interaction as was derived from the comparison with results obtained with the full Hamiltonian.

As we can see the result is a half-metallic ferromagnetic interface indeed, so we conclude that we *can* derive half-metallic properties by building a multilayer system of a semiconductors and a ferromagnetic metal.

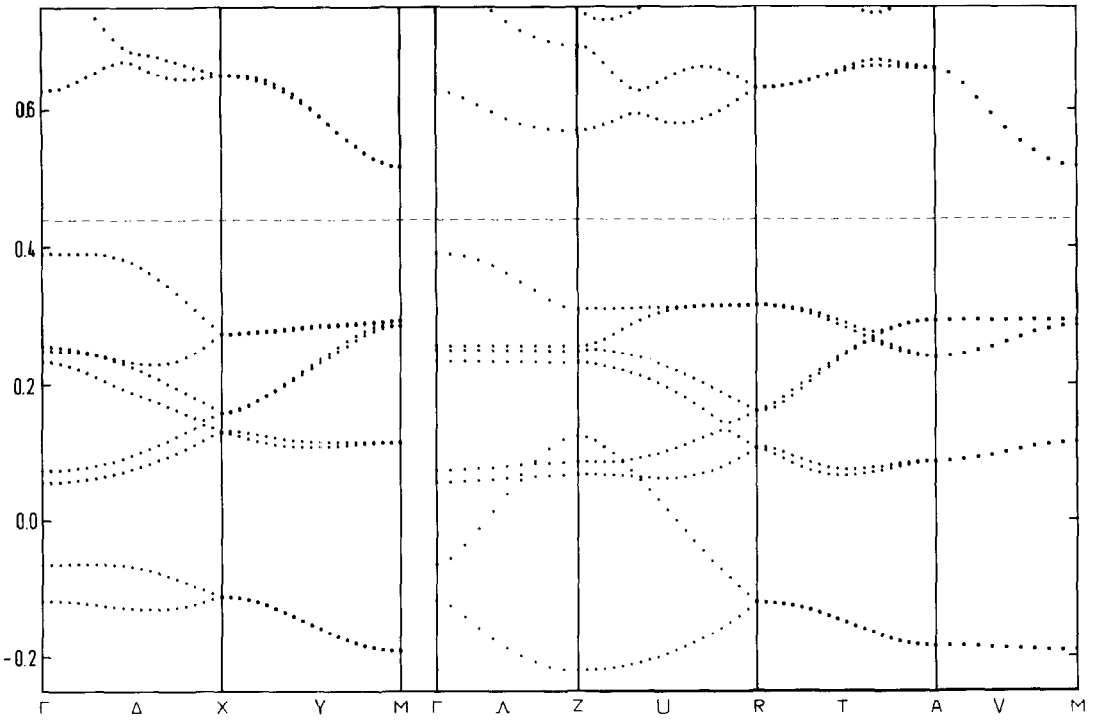

Fig. 2. The band structure of litharge (low temp. PbO).

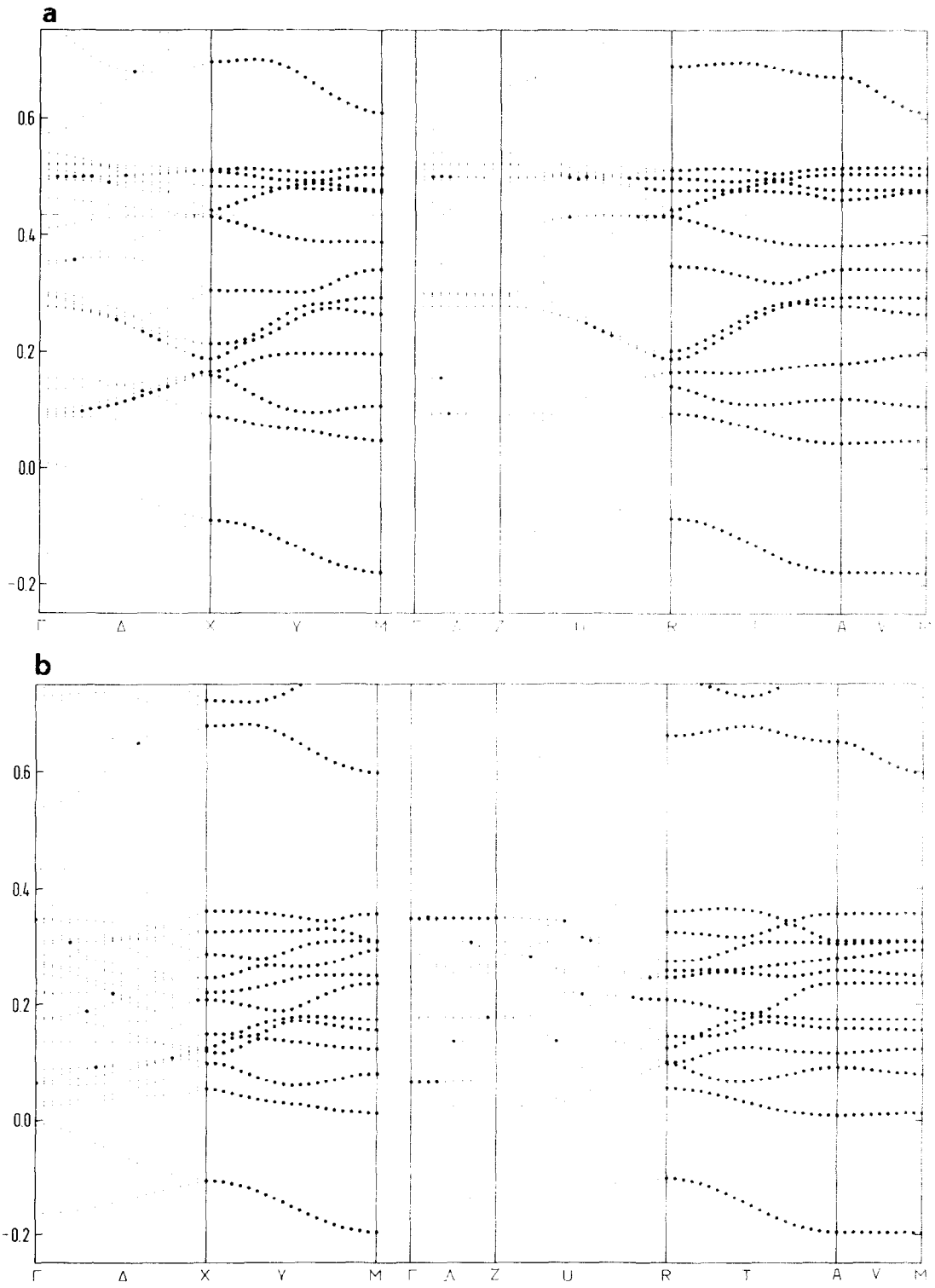

Fig. 3. Majority and minority spin direction band structure for PhO/Fe multilayer. For the purpose of this plot the L_+S_- and L_-S_+ operators were omitted, introducing small differences with the fully relativistic calculations.

2. The prospect of finding a half-metallic antiferromagnet

One of the possible applications of half-metallic magnets is as a source of spin-polarized electrons. Spin-polarized photoemission in NiMnSb does not give 100% spin-polarized electrons at threshold [15]. This observation is most likely due to either surface segregation or final-state effects. (The fact that the ground state is half metallic does not guarantee that the highly excited state as probed by photoemission is also half metallic.) Recently [16], the half-metallic ferromagnet CrO_2 [7] was successfully applied as a source of spin-polarized electrons in a scanning tunneling microscope (STM). (The fact that the conductor CrO_2 shows no states of either spin direction at E_f in photoemission [17] we attribute again to a final state effect [18].) The prospect of a spin-polarized scanning tunneling microscope (SPSTM) is exciting indeed. It could develop as a tool for studying occupied and unoccupied states close to E_f as a function of spin, complementary to photoemission and BIS measurements which have been so useful up till now. The advantage of the SPSTM would be that it will not perturb the system under study as much as high-energy spectroscopy does. However, there is a drawback. The possibility to study a system depending on spin is most relevant for magnetic systems, which unfortunately will be perturbed magnetically by the presence of a permanent magnetic tip a few angstroms away in the SPSTM set-up. This problem could be circumvented if we were able to design a half-metallic antiferromagnet, i.e. a system *without* a spontaneous magnetisation but *with* 100% spin polarization of the charge carriers at E_f. Such a material seems exotic, but we will see that it is quite possible – in principle at least.

The reason for this optimism is the following observation. First, it is important to realize that the spin-magnetic moment of a HMF is an integral number. This follows straight forwardly from the half-metallic nature: since one spin direction is semiconducting it has an integral number of occupied states. Since the total number of electrons is integral, the number of electrons for the metallic spin direction is necessarily also integral, as well as the difference of the number of electrons for the two spin directions – which is the spin-magnetic moment (at least for the purpose of this discussion).

In NiMnSb this number is 4, with the magnetic moment almost completely localised on Mn. The fact that CoMnSb is a HMF [4] originate from the fact that the electron it lacks compared to NiMnSb is completely donated by the metallic spin direction. Hence a reduction of the magnetic moment from 4 to 3.

In the following discussion we will consider the substitution of Co in CoMnSb by other 3d elements Fe, Mn and Cr. It has to be emphasized here that although most of these compounds do form with the given stoichiometry; they do not crystallize in the Heussler Cl_b structure, the structure for which the calculations on which this chapter relies have been performed. Substitution of Co by Fe would – if half-metallic behaviour persists – lead to a reduction of the magnetic moment from 3 to 2. The fact that this is indeed what happens comes from FeMnSb adopting a more complicated magnetic structure: it orders ferrimagnetically with the moment on Mn($3\mu_B$), antiparallel to the moment on Fe($1\mu_B$). In this way a net magnetic moment of only $2\mu_B$ results with at the same time higher local magnetic moments as would be possible in a ferromagnetically ordered half-metallic system. This is the result of a new contribution to the exchange coupling: the only possible way for FeMnSb to have seizable moments and maintain the energy gain of the energy gap for one spin direction is to order ferrimagnetically. The ferromagnetic solution has a higher moment ($5.09\mu_B$) but also a higher total energy since it is a normal ferromagnet.

In the same spirit MnMnSb in the Heussler Cl_b structure is a ferrimagnet, half-metallic with a net moment of $1\mu_B$. In going to CrMnSb the moment is reduced by another μ_B, hence CrMnSb is the half-metallic antiferromagnet we were looking for (fig. 4). In a sense, one could consider CrMnSb as an accidental antiferromagnet because the cancellation is not due to a symmetry relation between sites with up and down spins, but the moments on Cr are cancelled by the moments on Mn on different crys-

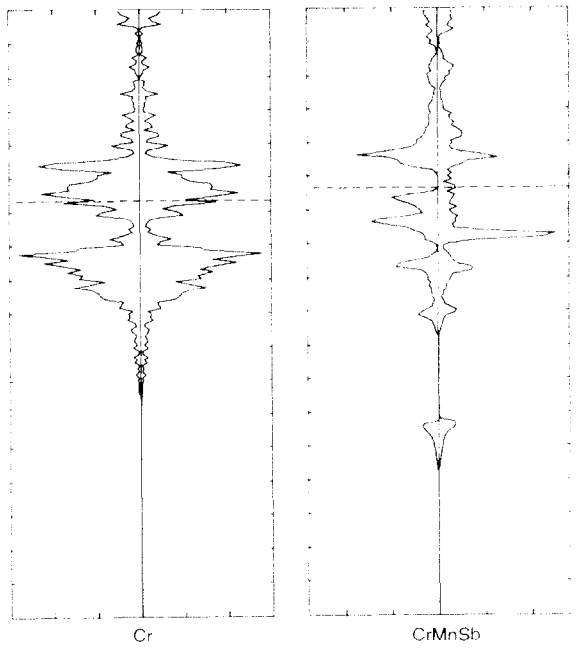

Fig. 4. Density of states of a classical antiferromagnetic (Cr) and of the half-metallic anti-ferromagnet CrMnSb in the Heussler Cl_b structure.

tallographical sites. The fact that this cancellation is complete is inherent to the half-metallic properties of CrMnSb: the integral magnetic moment is 0 here. Another important difference with conventional antiferromagnets is shown in the density of states curves at fig. 4. The electronic structure for the two spin directions in CrMnSb is completely asymmetrical with respect to the spin direction. It should be stressed, that the actual crystal structure of CrMnSb is much more involved and probably *not* half-metallic [19]. The important conclusion, however, is that at least in principle materials with 100% spin polarisation at E_f and no net magnetisation can exist!

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